Sodium Borohydride/Hydrogen Peroxide Fuel Cells For Space Application

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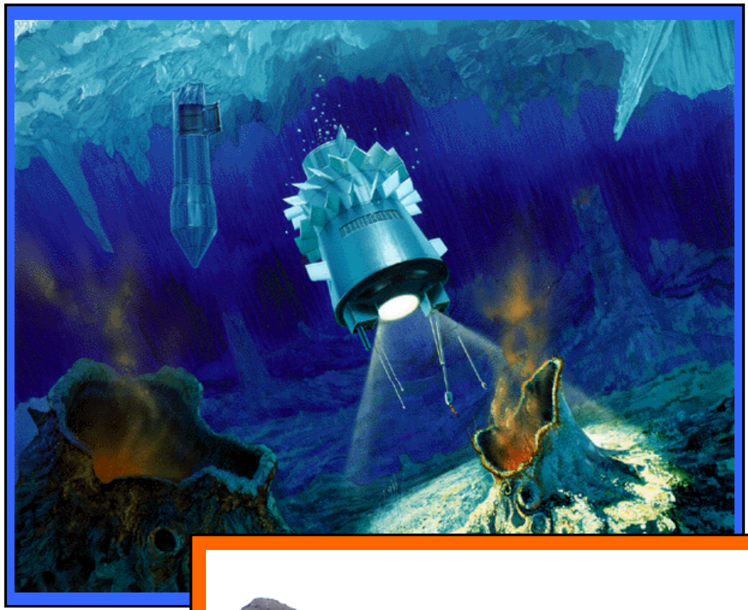
Presentation Outline

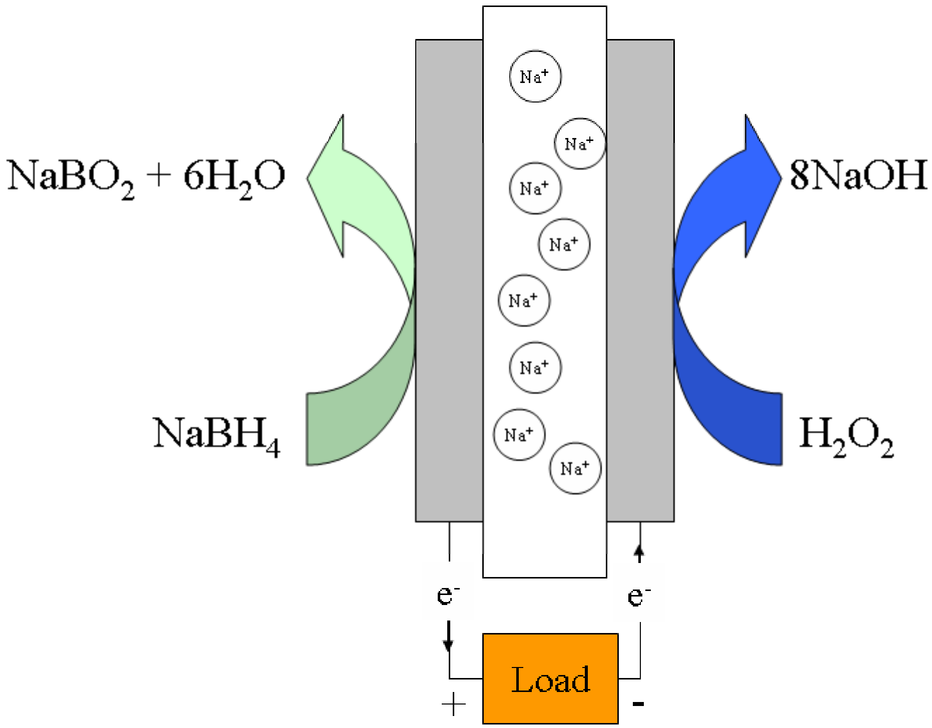
- Motivation
- The Sodium Borohydride Fuel Cell
- Sodium Borohydride Fuel Cell Test Stand
- Fuel Cell Comparisons
- MEA Performance
- Anode Polarization
- Electrode Analysis
- Conclusions

Hydrogen Peroxide Fuel Cell Systems



- Hydrogen peroxide can be used as an alternative oxidant for PEM based fuel cells in any application which can see a limited amount of free convection air.
- The sodium borohydride/hydrogen peroxide fuel cell offers distinct advantages:
  - Theoretical energy density: 2500 Whr/kg
  - Simplified thermal handling, liquid reactants

The Sodium Borohydride/Hydrogen Peroxide Fuel Cell



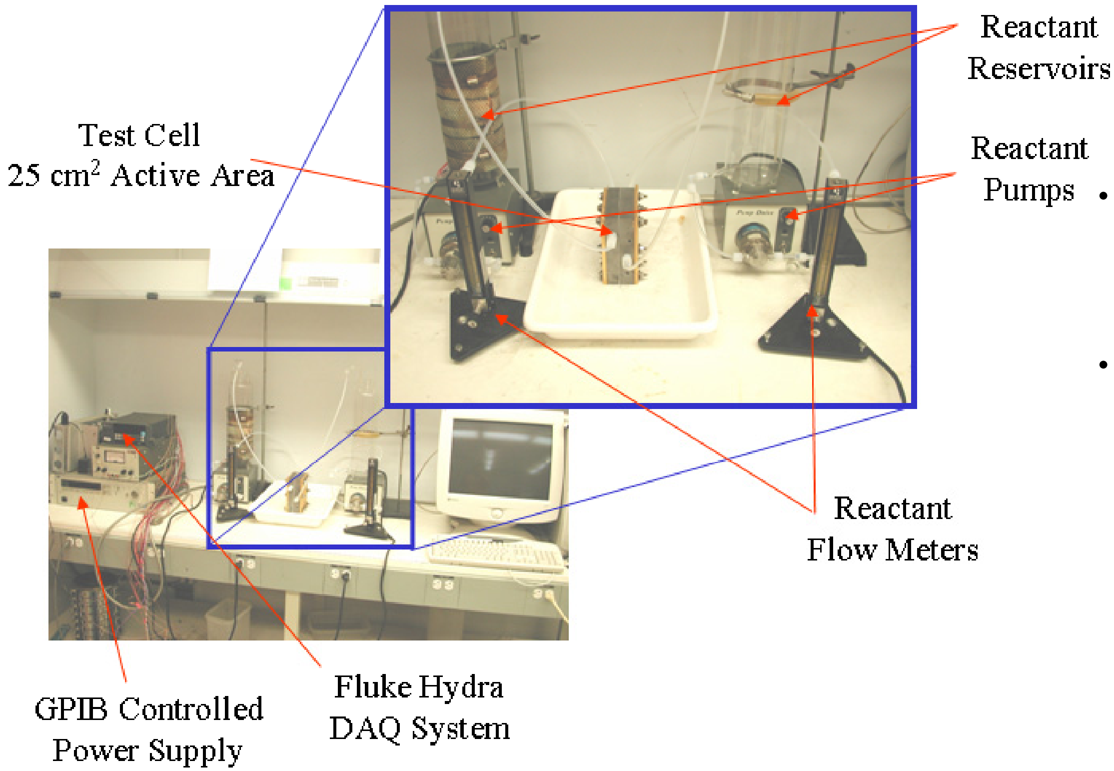
- Benefits of hydrogen peroxide as an oxidant
  - Higher current density from larger oxidizer mass density
  - Single-phase transport on the cathode side of FC increases reaction rate
- Benefits of sodium borohydride as a fuel
  - Sodium and Borate do not react electrochemically: neither pass through the PEM and both stay at anode side
  - NaBH4 is 30-40% soluble in water: can be used as a liquid directly at the anode, promising higher current density and efficiency
- Waste heat removed by oxidizer and fuel both in liquid form, giving better cooling

Anode: $NaBH_4 + 8Na^+ + 8OH^- \Rightarrow NaBO_2 + 6H2O + 8Na^+ + 8e^-$ $E^o = -1.24$ V[1]

Cathode: $8Na^+ + 8e^- + 4H_2O_2 \Rightarrow 8Na^+ + 8OH^-$ $E^o = 0.95$ V

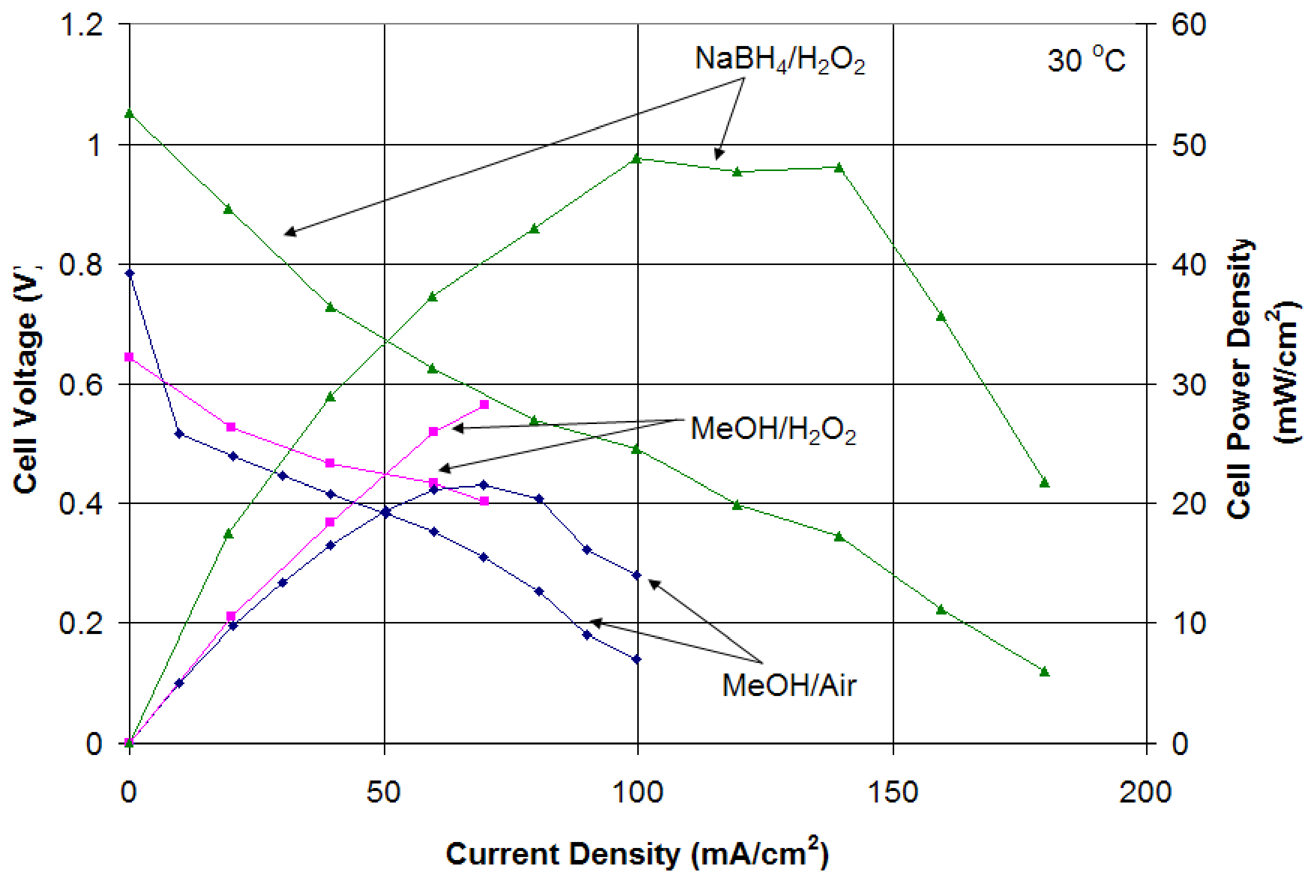
Cell: $NaBH_4 + 4H_2O_2 \Rightarrow NaBO_2 + 6H2O$ $V_{cell} = 2.19$ V

$NaBH_4/H_2O_2$ Fuel Cell Test Stand



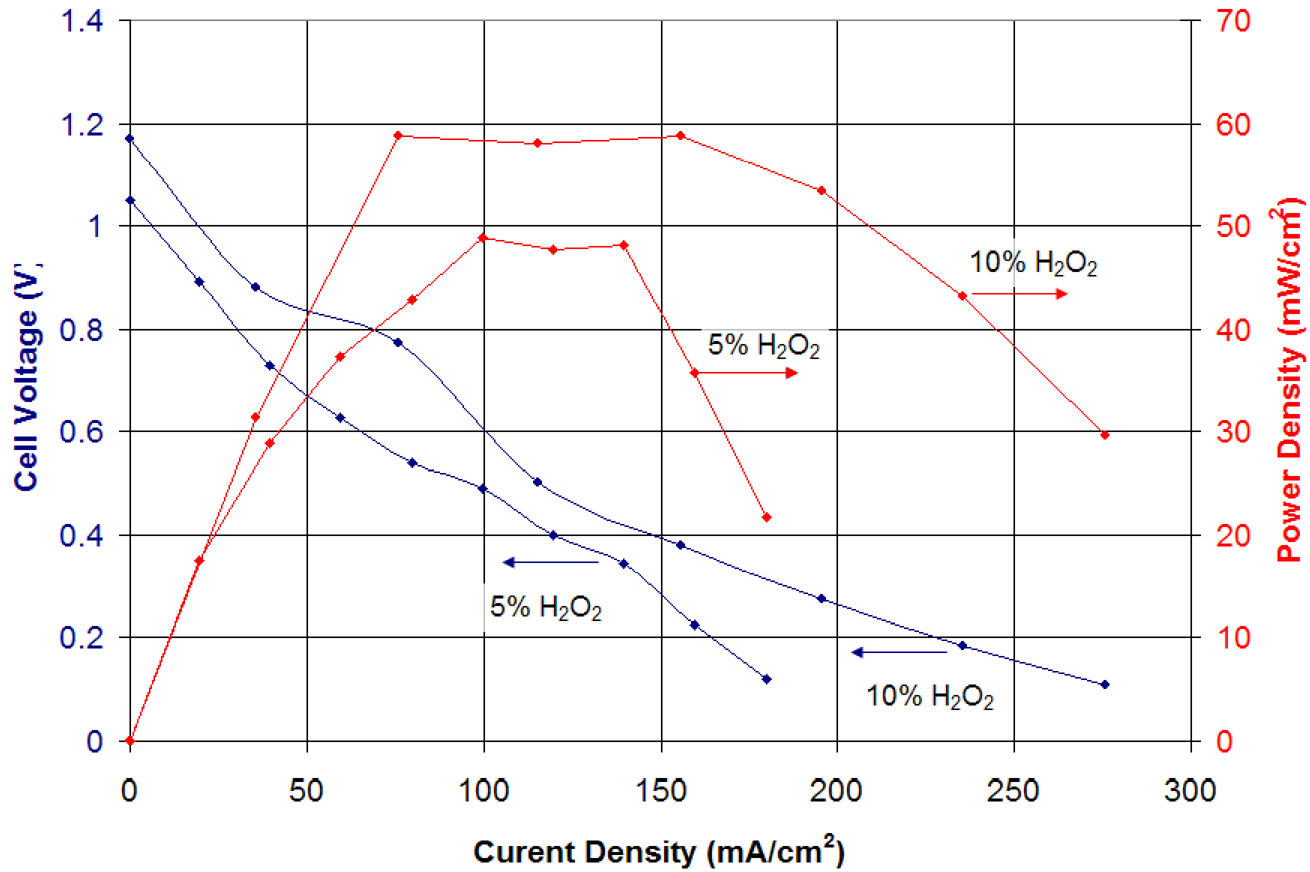
- MEA Fabrication Technique
  - Fabricated via a JPL direct deposit technique
  - Catalyst is deposited onto the PEM
  - Electrodes are hot pressed on the catalyzed PEM
- MEAs Fabricated
  - Pd-Pt (Anode-Cathode)
  - Pt-Pt
  - Au-Pt
- Reactant Specifications
  - Fuel: 5 to 10% $NaBH_4$ (Alfa-Aesar)
  - Oxidant: 5 to 10% H_2O_2 stabilized -CMOS grade solution (J. T. Baker)
  - All solutions were diluted in a 10 NaOH solution made with 18.2 mΩ water. (J. T. Baker)
  - Operating the cell with sodium hydroxide in both the anode and cathode compartments eliminates the sodium gradient across the Nafion membrane

Methanol-Based Fuel Cell Performance Comparison



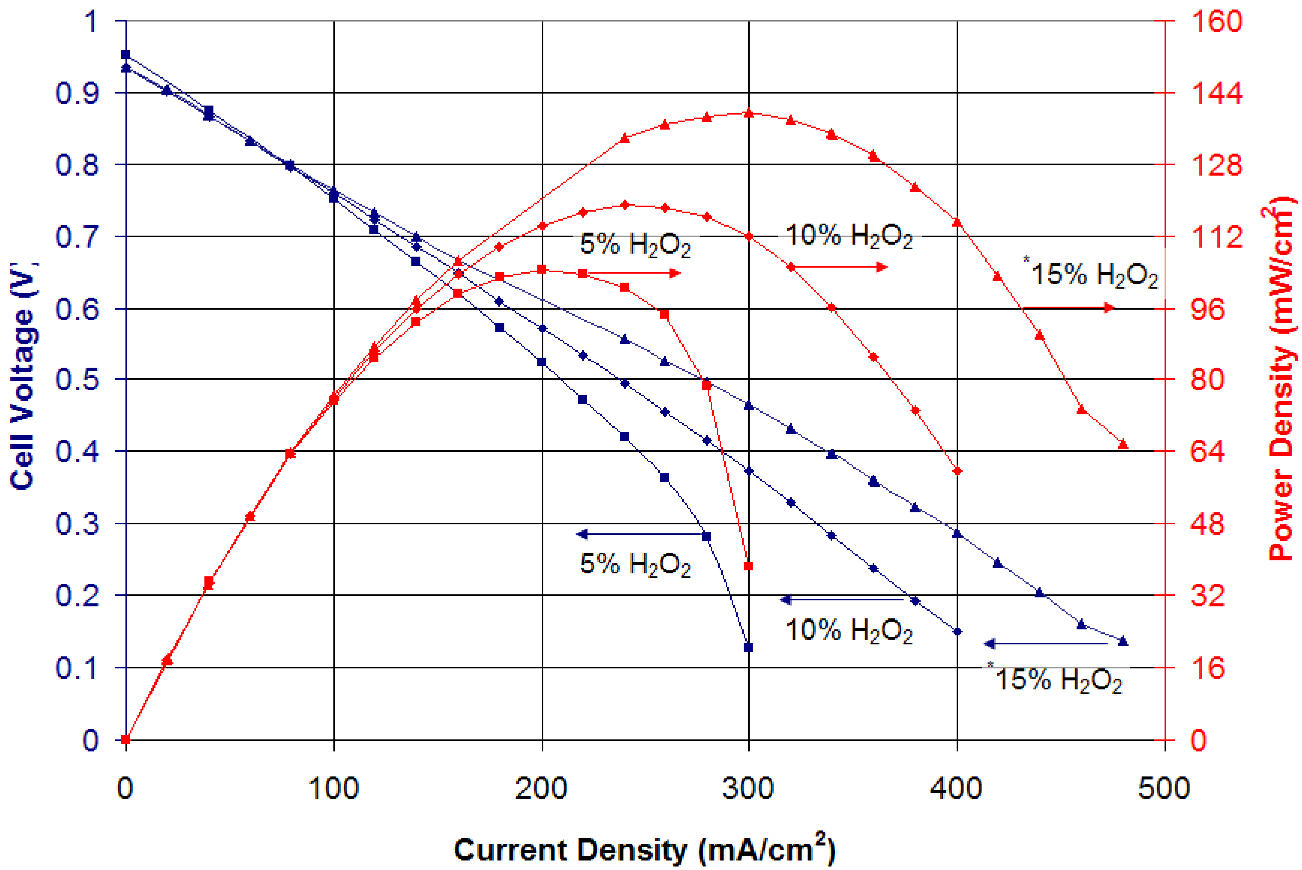
- Comparison of liquid-feed direct oxidation fuel cells at room temperature and ambient pressure operation.
- The maximum power density measured for the sodium borohydride/hydrogen peroxide system, at 30 °C, is 48 mW/cm^2. These values are higher (>2x) than that of a methanol/hydrogen peroxide system operated under similar conditions.

Current-Voltage Characterization as a Function Oxidant Concentrations, Cell Operating at 30 ^{o}C, Pd Anode



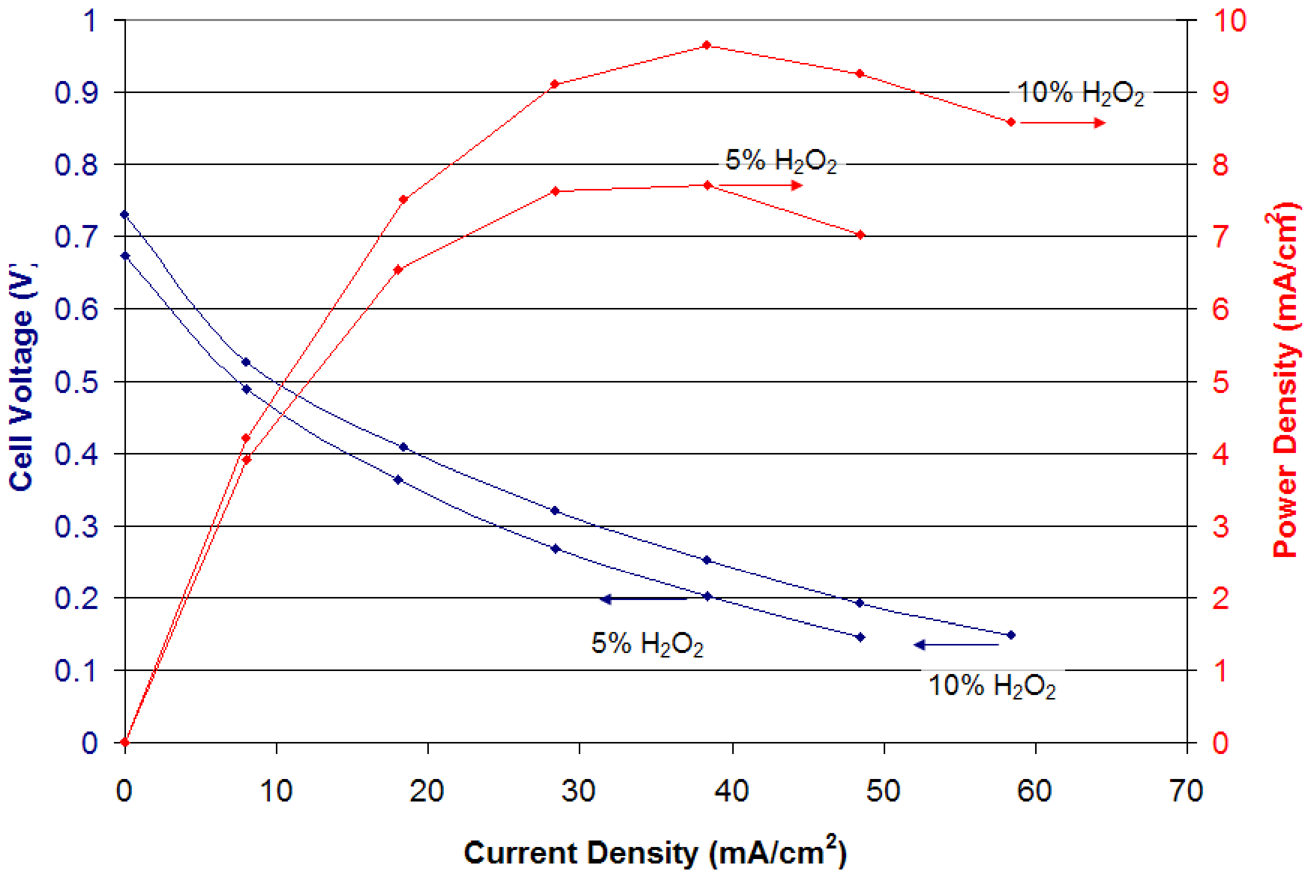
- Cell peak power density increases by 22% as the hydrogen peroxide concentration increased from 5 to 10%

Current-Voltage Characterization as a Function Oxidant Concentrations, Cell Operating at 40 °C, Pt Anode



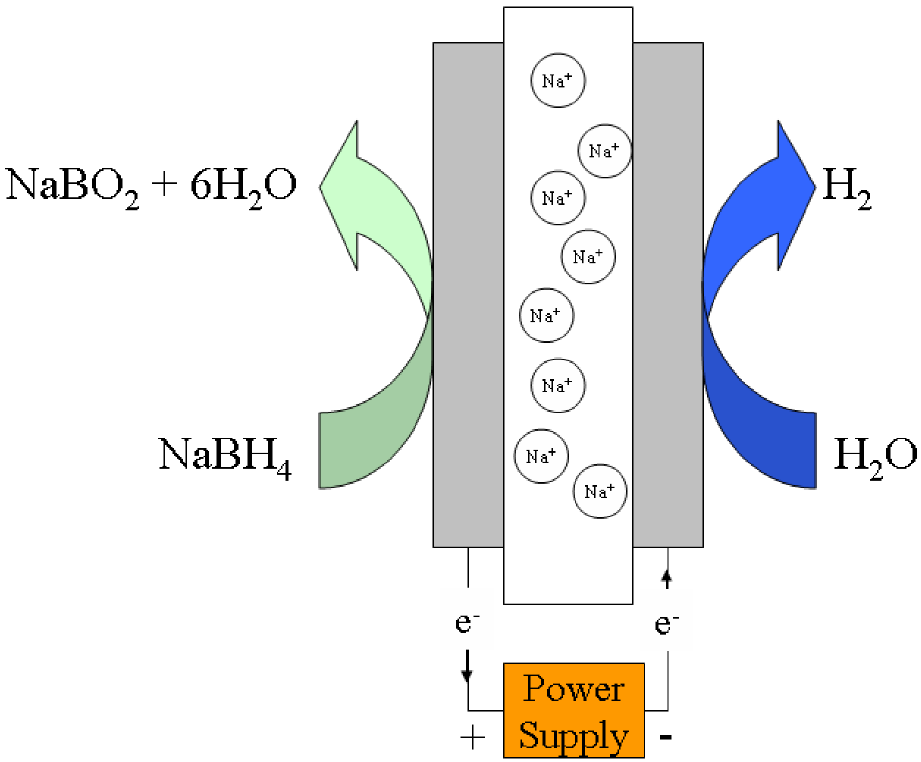
- Cell peak power density of 140 mW/cm^2 possible at high hydrogen peroxide concentrations

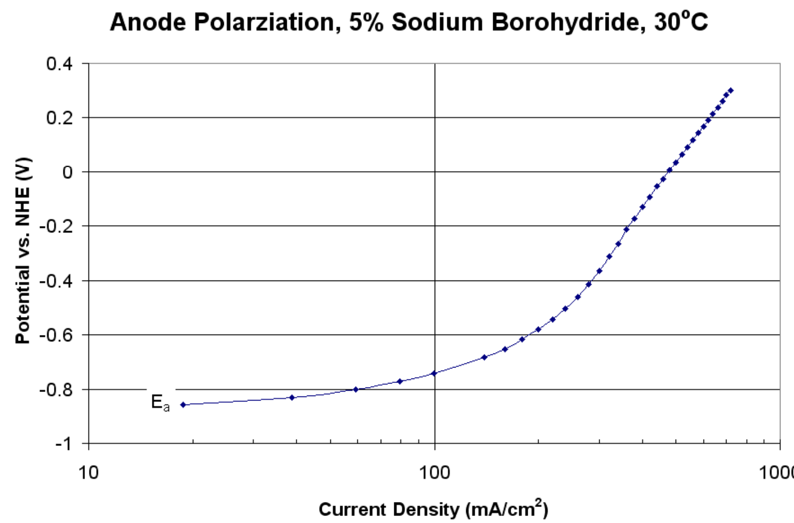
Current-Voltage Characterization as a Function Oxidant Concentrations, Cell Operating at 40 °C, Au Anode



- Gold anode produces lower power

Anode Polarization Technique





Electrochemical Reaction

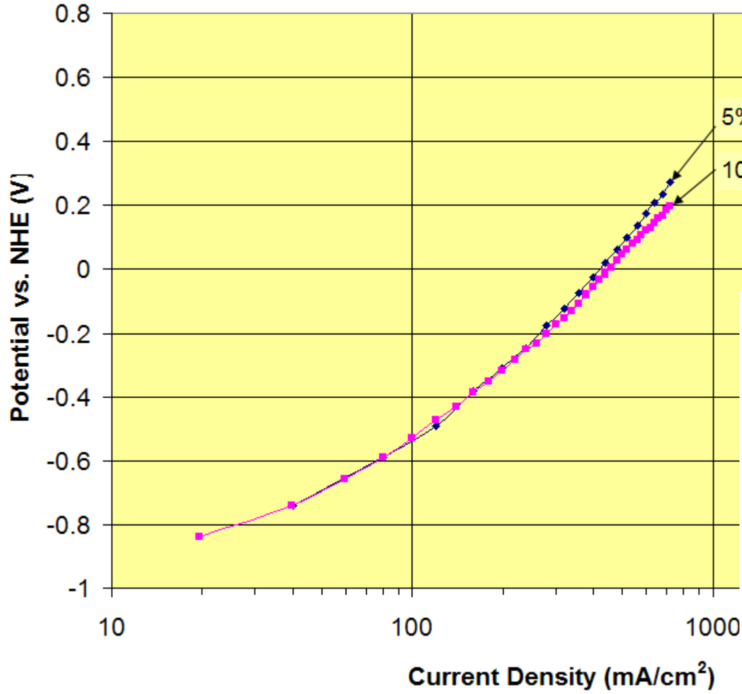
Anodic: $NaBH_4 + 8Na^+ + 8OH^- \rightarrow NaBO_2 + 6H2O + 8Na^+ + 8e^-$

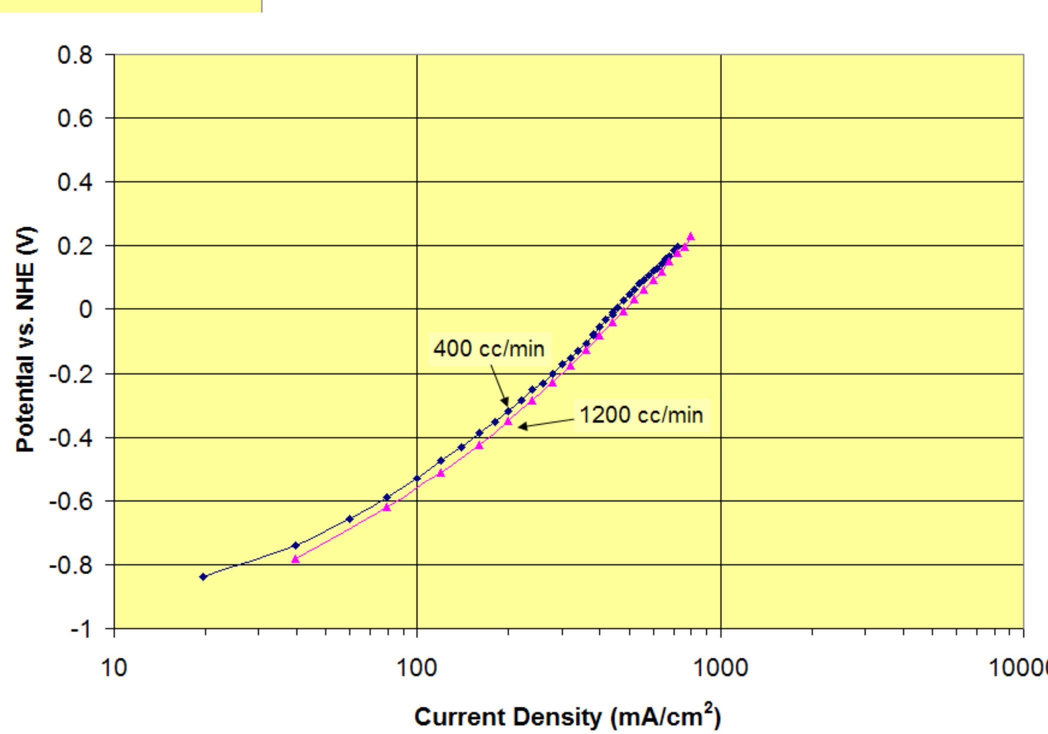
Cathodic: $8Na^+ + 8e^- + 8H2O \rightarrow 4H_2 + 8Na^+ + 8OH^-$

Test Set-up

- A solution of sodium hydroxide, of the same concentration used to dilute the fuel, is introduced into the cathode compartment of the fuel cell. This eliminates the sodium gradient across the Nafion membrane.
- When current is pulled from the cell, the sodium borohydride is oxidized at the anode and the product hydrogen formed at the cathode allows this electrode to function as a dynamic hydrogen electrode.
- The sodium hydroxide solution is used to sweep product hydrogen away from the cathode and maintain the pH of this electrode at the same level of the anode.
- When the cell is polarized, the resultant curve will be $\mathbf{E_a}$ vs. current density of the cell.

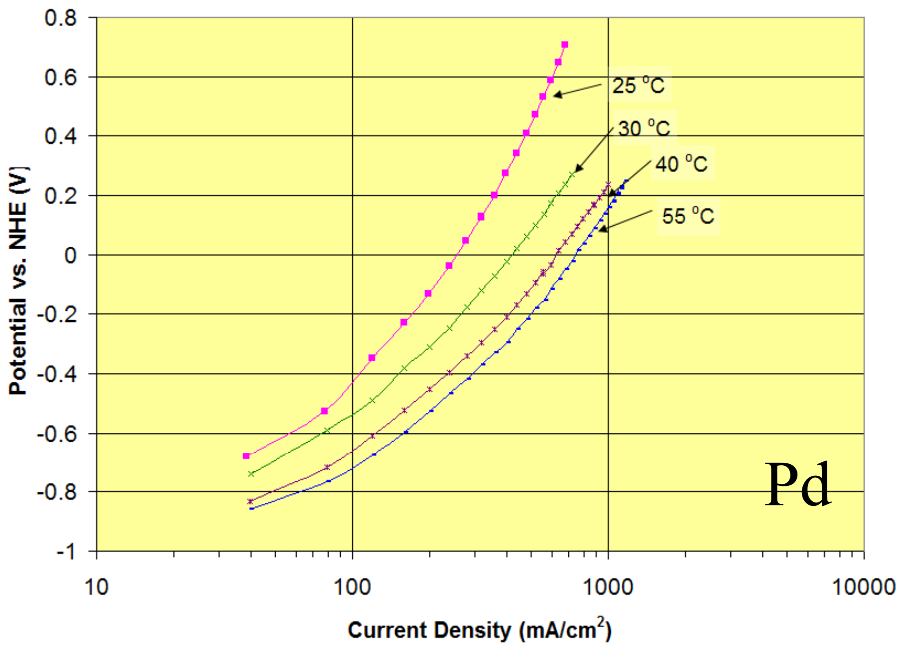
The Effect of Fuel Concentration on Anode Polarization Performance

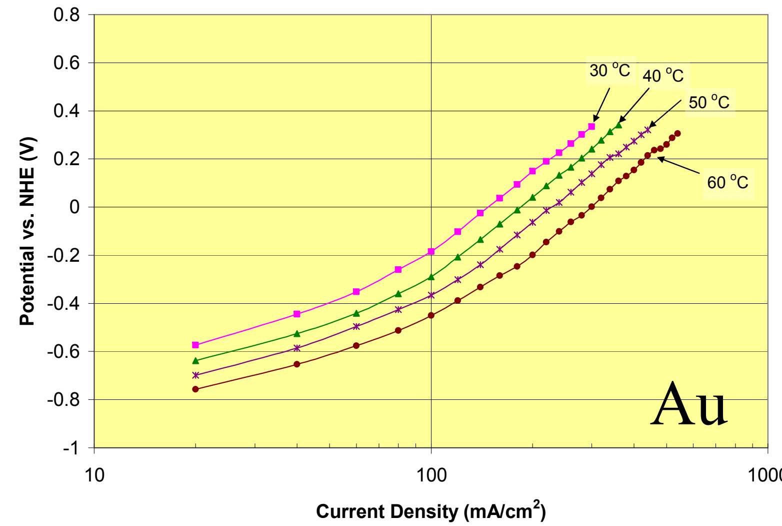


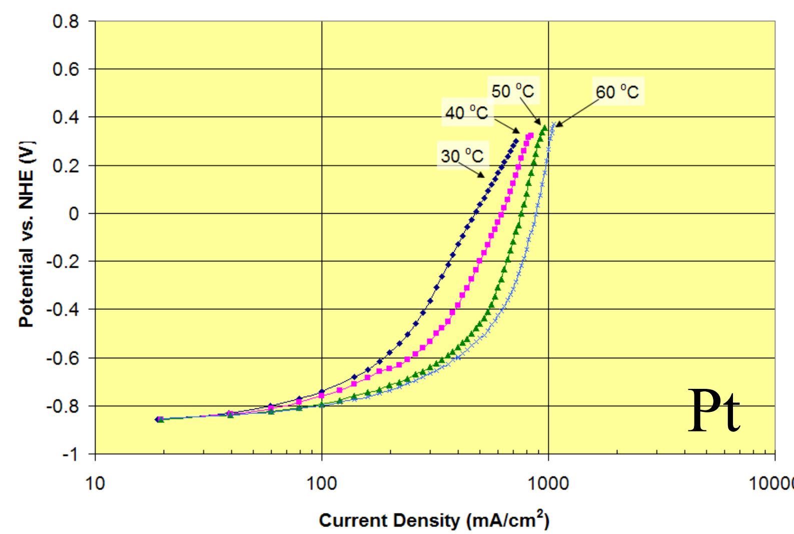


- The polarization plots, as a function of concentration, slightly diverge at current densities above 300 mA/cm^2
- Fuel flow rate has a minimal effect on anode performance

Anode Polarization Performance as a Function of Temperature



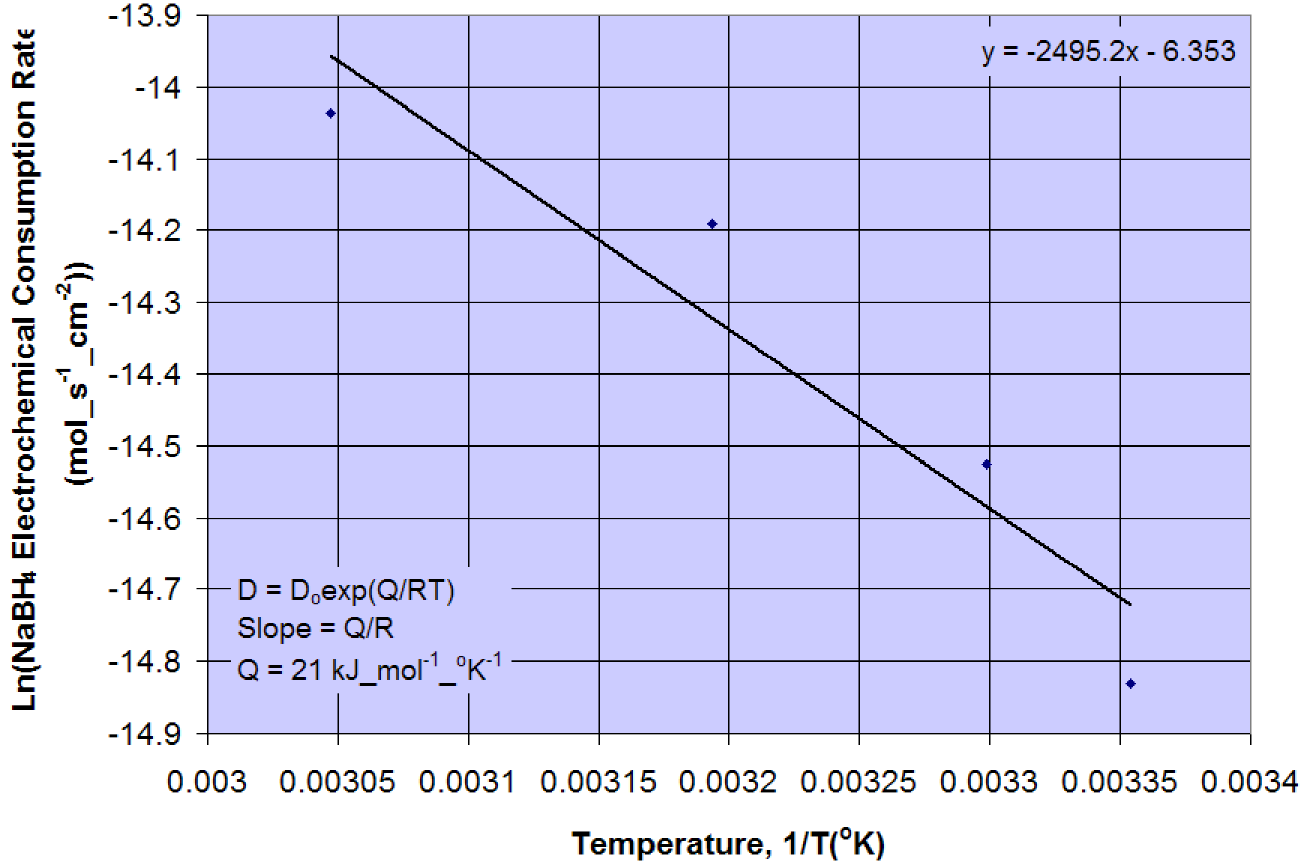




•Tafel slopes for each of the anode polarization plots are in the range of a 100's of mV/decade

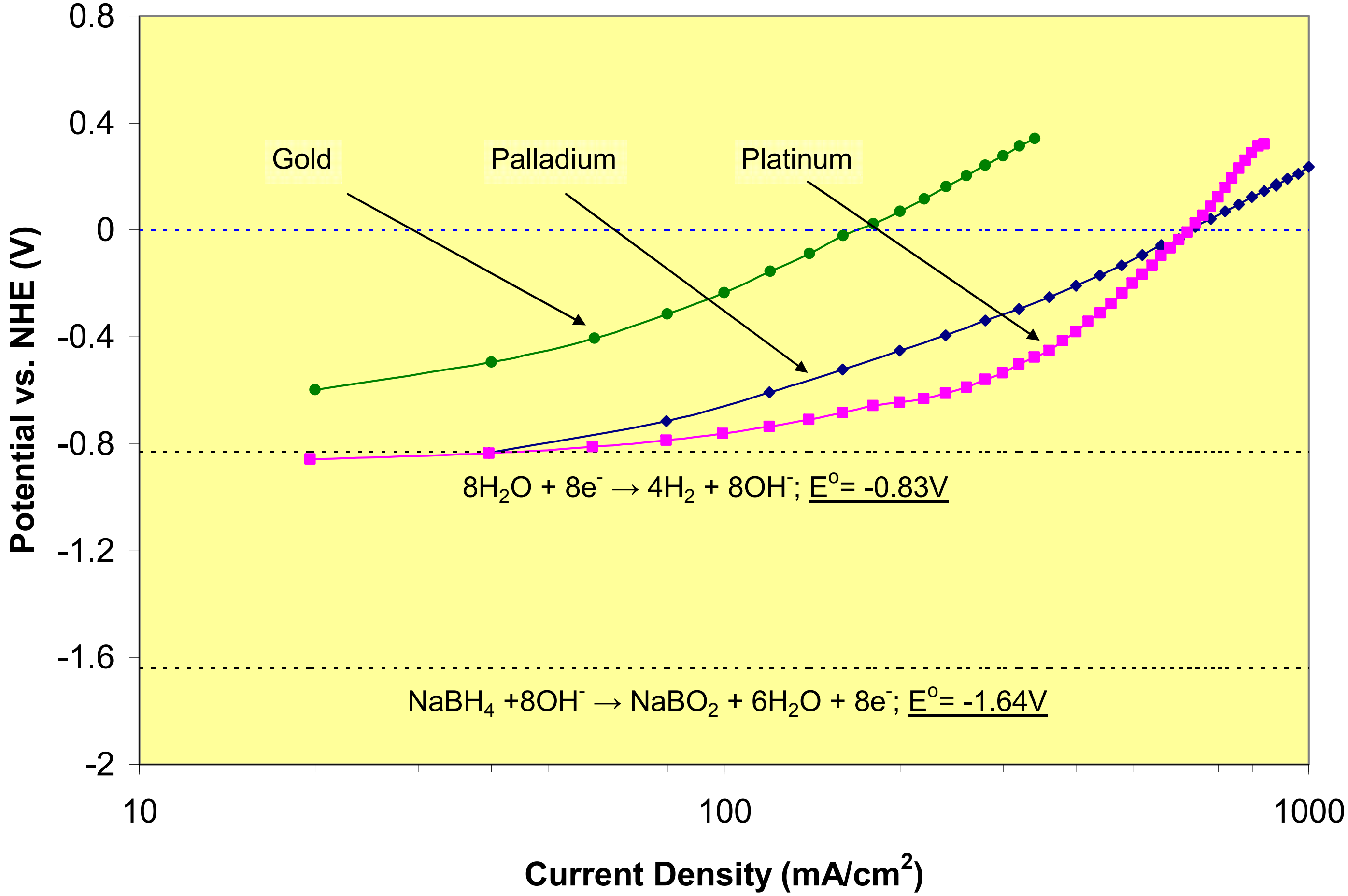
•A process beyond charge transfer might be present during the electrochemical oxidation of the sodium borohydride fuel on the palladium catalyst/carbon paper

Activation Energy for the Platinum/Carbon Paper Electrode



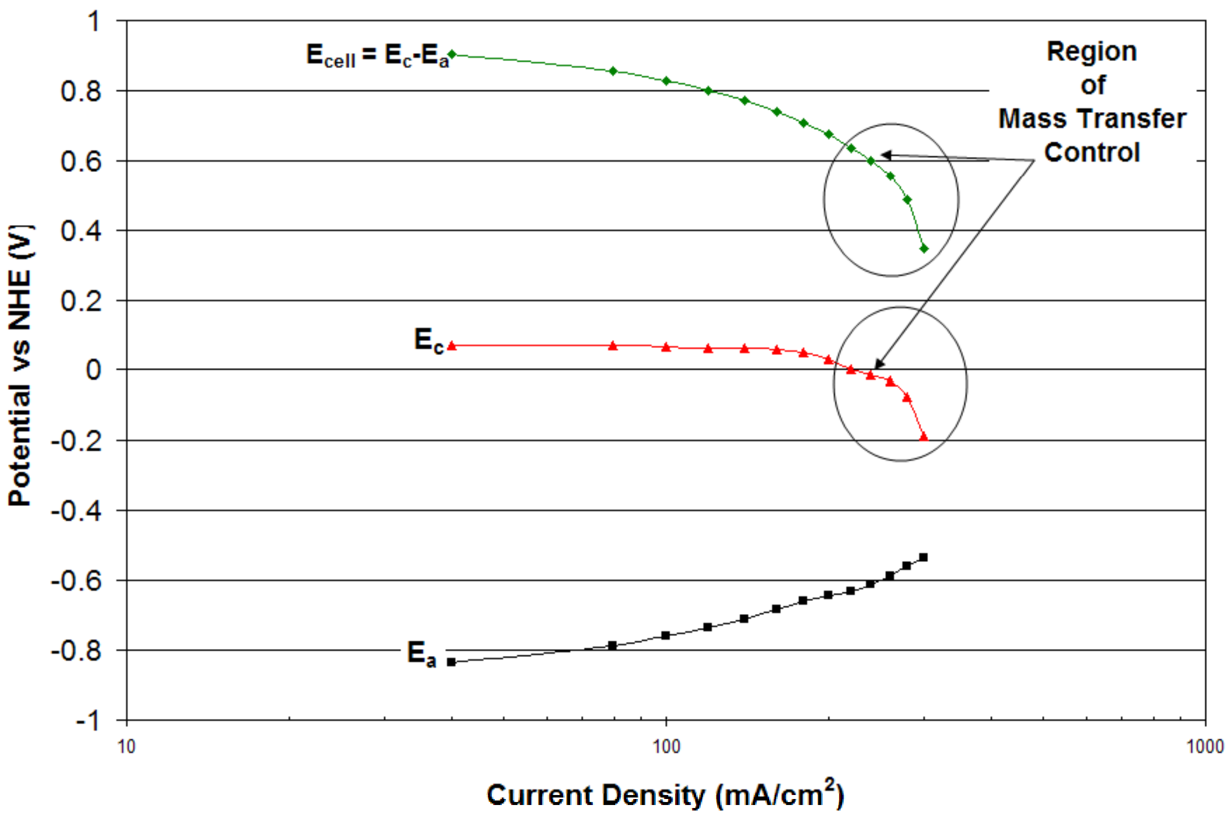
- Activation energy for the reaction on the platinum catalyst/carbon paper structure is calculated to be 21 kJ/(mol oK)

Anode Polarization Analysis, Cells Operating at 40 °C



- An ideal catalyst for the oxidation of sodium borohydride would operate at a potential below -0.83 V vs. NHE and preferably as low as -1.64 V vs. NHE

Polarization Analysis for a Cell Operating at 40 °C

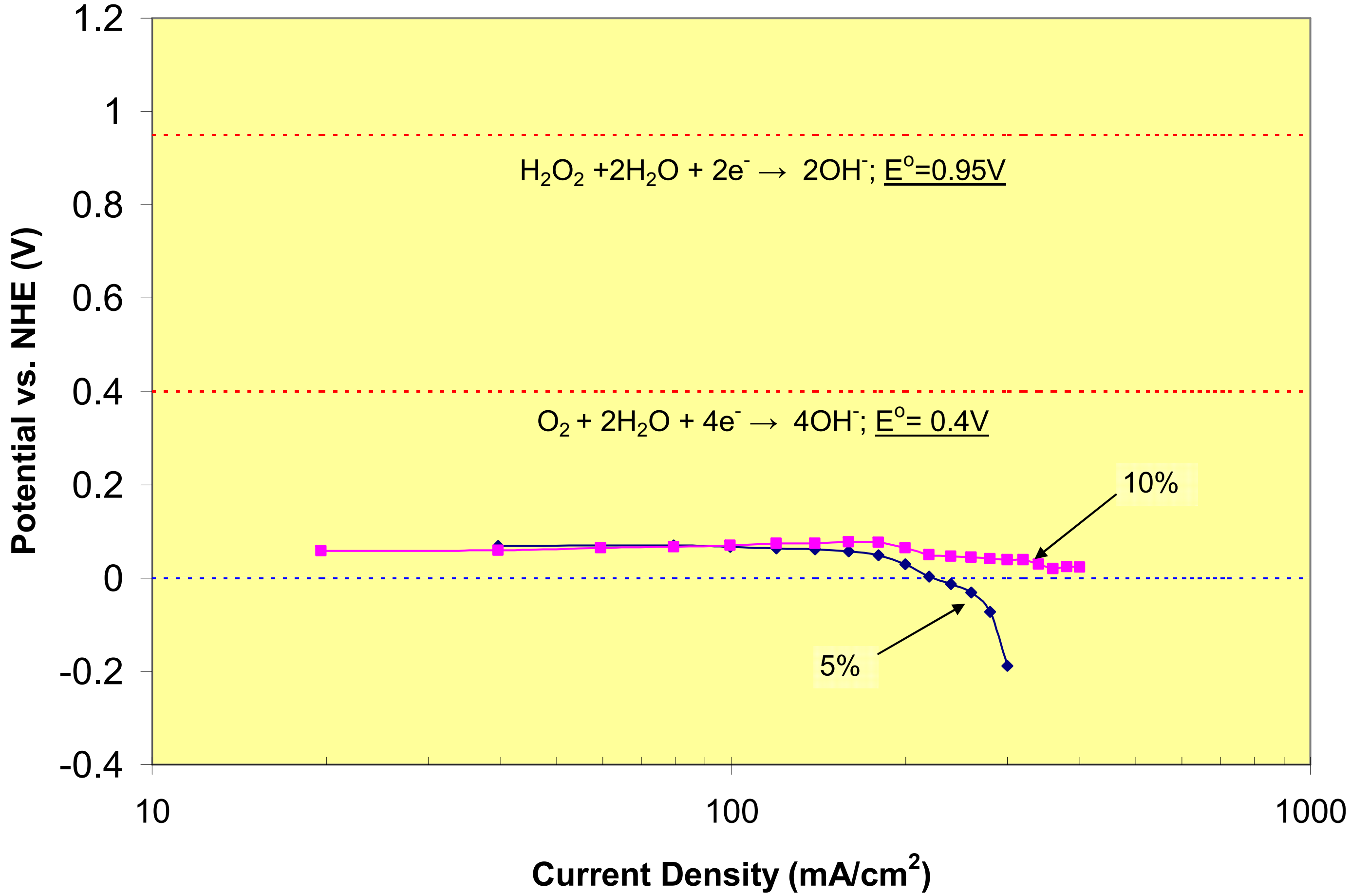


- $\mathbf{E_{cell}}$, at any oxidant concentration and flow rate, can be added to $\mathbf{E_a}$ at the same fuel molarity and temperature to get $\mathbf{E_c}$ corresponding to oxidant concentration and flow rate.

$$E_c = E_{cell} + E_a$$

- When $\mathbf{E_a}$ and $\mathbf{E_c}$ are plotted together as a function of current density, the kinetics of the reaction can be seen.

Cathode Polarization Analysis, Cell Operating at 40 °C



- For cell operation on 5% hydrogen peroxide, the cathode will become mass transfer limited for current densities greater than 240 mA/cm2

Conclusions

- The maximum power density measured for the sodium borohydride/hydrogen peroxide system, at 30 ^oC, was 58 mW/cm^2. These values are higher (>2x) than that of a methanol/hydrogen peroxide system operated under similar conditions.
- MEA data taken with the Anode Polarization Technique was useful in separating the anode and cathode performance
- Electrode polarization analysis revealed that both the anode and cathode of the cells were underperforming electrochemically.
- The cathode performance was just above 0 V vs. NHE which is well below that expected values for oxygen and hydrogen peroxide in alkali environments.
- To improve the present system, catalyst that are more selective towards the oxidation of sodium borohydride and more selective towards the reduction of peroxide are required. In light of previous work on the methanol/hydrogen peroxide system, a cathode catalyst has the secondary requirements of being tolerant to $NaBH_4/NaBO_2/NaOH$.

Acknowledgements

The work presented here was carried out at the Jet Propulsion Laboratory, California Institute of Technology for the National Aeronautics and Space Administration. Studies on sodium borohydride/hydrogen peroxide fuel cells were performed under a program led by Professor George Miley of the University of Illinois, Urbana-Champaign